

Apparatus for Determination of Pressure-Density-Temperature Relations and Specific Heats of Hydrogen to 350 Atmospheres at Temperatures Above 14 °K*

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(June 20, 1961)

Method and apparatus are designed for more rapid determination of accurate, closely-spaced, PVT and specific heat data than realized by previous procedures. A sequence of pressure-temperature observations at nearly constant density is made by a modified Reichsanstalt method. Temperatures of the essentially adiabatic piezometer are regulated by electric heating under control of the measuring thermometer. Instruments for measurement and control are integrated with a high-pressure calorimeter for compressed liquid and fluid. Calorimetric experimentation is accelerated by use of an electronic battery for the calorimetric heat supply and of a d-c power regulator developed for automatic shield control. Details are given of the PVT calibrations, adjustment computations, and comparisons with independent data.

1. Introduction

The high-density physical properties of hydrogen are needed for technological applications [5, 10]. Thermodynamic functions may be computed from certain thermal data combined with a wide range of precise mechanical properties (PVT) and vapor-pressure data [1, 2, 3, 9]. The purpose of this paper is to describe the essential features of apparatus used to obtain PVT data for parahydrogen from 16 to 100 °K and from 2 to 350 atm, and to obtain specific heats of compressed liquid and fluid in the same range. Advent of high-speed digital computers renders practical the handling of a large quantity of data, produced by closely-spaced observations with accelerated methods to be described.

2. Experimental PVT Method

The PVT method and its numerous calibrations are emphasized in preference to the better-known calorimetric techniques, outlined below. The popular Burnett method for PVT determinations [17] is not suitable for compressed liquids [9]. That of Holborn and coworkers [20, 21, 22], termed the Reichsanstalt method [2], involves essentially direct measurement of each variable. As employed by Michels and coworkers, a sample of fluid of known PVT behavior at normal temperature is confined in the piezometer and pressure gage system at that temperature. Pressure of the sample then decreases rapidly with temperature of the piezometer [25]. In the Ohio State University modification for gaseous states, adjustments for obnoxious volumes of capillary and gage were eliminated by placing a valve in the cryostat. This necessitated an independent de-

termination of the amount of sample following every P-T determination [24]. For liquid states they employed a boiling hydrogen thermostat. Successive small portions of the sample were released from the piezometer or "pipet" to obtain a series of isothermal P-v determinations from a given filling, each P-v point again requiring an independent volumetric determination [23].

Average time per determination is greatly reduced in the present method. Temperature of the nearly adiabatic pipet is varied to obtain a series of P-T determinations at nearly constant density. Temperatures are automatically controlled at exact, integral values, to permit handling the data as isotherms. Only one determination of the amount of sample is required following each experimental "pseudo-isochore". The portion of the total sample which was in the pipet during each P-T determination is calculated by subtracting the computed amounts residing simultaneously in capillary and diaphragm cell under those conditions. For this small adjustment, the known and estimated PVT behavior of normal hydrogen is employed.

With reference to figure 1, a sample of the experimental fluid is confined by valve C-4 to the following system: the heavy-walled copper pipet, the stainless "transition" capillary tube in the cryostat, the capillary tubes and valves at room temperature, and the pressure-sensitive diaphragm cell (N. P. D.). Volumes of these elements are calibrated independently. The latter transmits pressure of the fluid to the oil of a piston-type, deadweight gage. With reference to figure 2, liquid hydrogen refrigerant resides in the tank. The pipet is cooled strongly as required by liquid hydrogen reflux action from hydrogen gas introduced to the thin-walled, stainless steel "reflux" tube supporting the pipet. For automatic temperature regulation by electric heating, under control of

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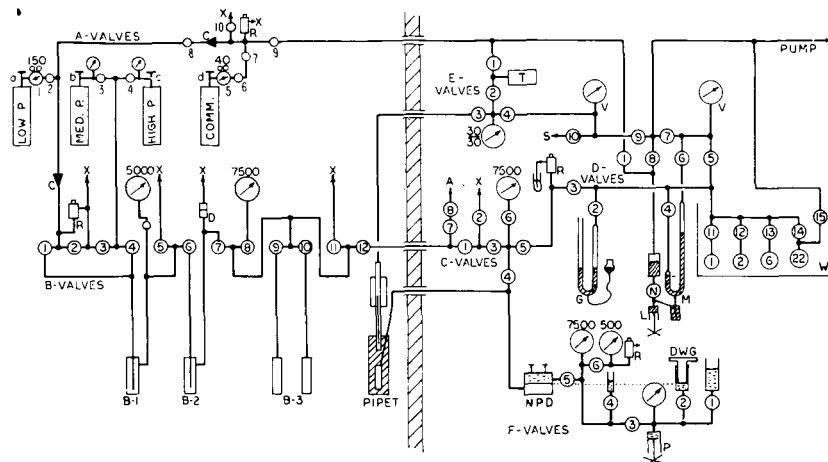


FIGURE 1. Pneumatic apparatus for PVT determinations.

- | | |
|---|------------------------------|
| A, Connection to thermal conductivity analyzer. | M, Precision manometer. |
| B-1, Absorbent bomb at 76 °K. | NPD, Null pressure detector. |
| B-2, Iron-oxide, ortho-para catalyst bomb at 19.6 °K. | P, Oil press. |
| B-3, Thermal pump bombs. | R, Relief valves. |
| C, Check valves. | S, Sampling connection. |
| COMM., Commercial hydrogen. | T, Reflux gas dose tank. |
| D, Bursting disk. | V, Phillips vacuum gauges. |
| DWG, Dead weight gage. | W, Water-bath thermostat. |
| G, Gas buret. | X, Exterior vent lines. |
| L, Mercury leveling screw. | |

the platinum resistance measuring thermometer, gas pressure in the reflux tube is reduced to provide controlled cooling by gas convection, aided by a copper rod suspended in this tube.

An experimental run consists of measurement of a sequence of pressure versus temperature points, beginning at the lowest temperature. The total quantity of confined fluid then is determined by releasing it as gas into volumetric system *D* of figure 1 and measuring *P*, *V*, and *T* at about normal conditions, accounting also for the gas remaining in all obnoxious volumes and in the pipet at this pressure. Experimental time required for filling and emptying the pipet is greatly reduced through capability of the commercial, null-pressure diaphragm instrument to withstand high-pressure imbalance without damage. About 30 points on a pseudo-isochore are determined routinely in 8 hr by 2 or 3 men.

3. Sample Preparation, Handling, and Analysis

By mass-spectral analysis, electrolytic hydrogen in clean steel cylinders at 2,000 psig contains less than 5 ppm helium and 100 ppm air, respectively. The preparation system on the left of figure 1 has three functions. Impurities are absorbed at 76 °K in B-1 on 20 ml of 1.6 mm diam extrusions of "molecular sieve" silica [71]. The paramodification of hydrogen is produced catalytically in B-2 at 19.6 °K on 10 ml of "30-100 mesh" particles of an iron oxide, batch 48-C, used in activity studies [72]. Small disks of sintered stainless steel retain the fine solids in their containers. Two stainless steel bombs, B-3, each of about 20 ml capacity, may be immersed in liquid nitrogen to provide a two-stage, thermal pump for

boosting the parahydrogen pressure. Solidification of hydrogen at the catalyst is avoided by placing the catalyst ahead of these pumps in the train. The hydrogen cylinders, preparation system, liquid hydrogen transport Dewar, cryostats and vacuum pumps are separated from the instrument room by an explosion-proof wall. Valve manifold C in the instrument room uses a bourdon gage as a doser for filling the pipet to selected densities and for controlling release of the pipet sample to the gasometer system *D*.

Systems B and C of figure 1 are assembled with 1/16-in. o. d. stainless steel tubing and high-pressure midjet valves with solid stems and polytetrafluoroethylene O-ring packings. Shop-fabricated gage connectors force a small, drilled, metal cone against a conical recess on the gage stem. This special fitting is necessary to avoid contamination of the gas. Bourdon gages for hydrogen must be phosphor-bronze, beryllium-copper, or type 316 stainless steel [75].

Analysis for parahydrogen is performed on gas bled from valve C-8 at 100 ml NTP/min through a thermal conductivity instrument [58]. Calibration depends upon parahydrogen produced independently. In preliminary studies the rate of conversion of para- to orthohydrogen in the pipet at pressures up to 4,500 psi was in the order of one percent per day at 76 °K and 25 to 30 percent per day at 275 to 300 °K. The vapor pressure of parahydrogen was measured at the beginning of a number of PVT runs [66]. Following one of the routine, 8-hr PVT determinations, the presence of parahydrogen again was confirmed by a vapor pressure measurement.

4. Cryostat and Piezometer

Descriptions and summaries of low temperature techniques are available [11, 12, 13, 14, 38, 46].

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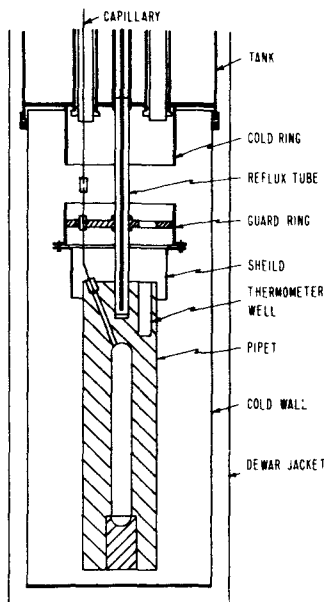


FIGURE 2. Piezometer region of PVT cryostat.
(Shield is misspelled in the above figure.)

Figure 2 shows a cross section of the lower portion of the cryostat. A 25-ml pipet sample cavity, 5/8-in. diam, is bored into a two-in. diam, solid copper cylinder 8.5-in. long. To avoid oxidation, the plug is brazed with helium in the cavity. Metal stress is about one half the internal pressure. Helical grooves on the cylinder carry a 32-gage, 500 Ω constantan wire heater. The platinum thermometer is tinned and cast into the pipet with Rose's alloy. Above the pipet on the supporting, thin-walled, stainless steel tube, a guard ring thermally tempers electric wires leading to and wound on the pipet; the ring is automatically controlled at pipet temperature by a gold-cobalt versus copper thermocouple [40, 44] and a 36-gage, 100 Ω constantan wire heater. A cold ring, integral with the refrigerant tank, tempers electric wires entering from room temperature. Before it was mounted and wound in the cryostat, the bundle of 36-gage, low-level wires was constructed as a unit with all wires lightly varnished together parallel in a plane to insure good thermal contact on the rings. The levels of cooling through the reflux tube which do not disturb the temperature-versus-pressure relationships are determined experimentally. About 10 milliwatts cooling normally is used.

An evacuable copper can, soldered to the tank with Rose's alloy, encloses the pipet. A Dewar vacuum jacket immersed in an open Dewar of liquid nitrogen protects the can and the tank. A permanent liquid hydrogen transfer line with built-in valves enters the cryostat refrigerant tank through an O-ring seal, with the amount of refrigerant in the tank shown by an electronic level-indicator instrument. Suitable valves and safety devices on the vent from the tank permit the use of a rotary oil pump to attain the triple-point temperature of the refrigerant.

5. Measurement of Sample Volume

5.1. Normal Pipet Volume

This volume is required for computation of density. By ignoring the adjustments contained in eqs (10.1-1) and (10.3-1) there is obtained the rough approximation for sample density,

$$\sigma \approx (P_m/RT_b)(V_g/V_o), \quad (5.1-1)$$

where P_m , T_b and V_g refer to the gasometry system and V_o is pipet volume. Whereas the ratio V_g/V_o dominates the computation of eq (10.3-1), it is a practical convenience to perform absolute calibrations.

The pressure and temperature-dependent volume of the pipet is required. Connection to the pipet cavity is made with a 3-in. length of 0.35 mm stainless capillary brazed to the pipet drill hole, figure 2. The pipet was briefly tested to 8,000 psi. A midjet valve was attached to the capillary, the pipet evacuated, and freshly boiled water admitted to the pipet. The three determinations yielded an adjusted volume of 25.83 ± 0.016 cm³ at 25 °C. Volume at room temperature after mounting in the cryostat was determined by expanding hydrogen from the pipet at about 1,000 psi into the gasometer system of section 6. Seven determinations yielded adjusted volume 25.854 ± 0.037 cm³ at 25 °C. Following two series of high-density experiments for PVT data to 5,400 psi, low-density experimental results violated general, low-density, limiting gas behavior. Six redeterminations of pipet volume by gas expansion yielded normal volume 25.913 ± 0.009 cm³ relative to the gasometer volumes, in agreement with deductions from low-density behavior. The first series of PVT experiments is rejected, and the increase of molal volume by factor 1.00263 is applied to all other data. The annealed pipet is thus assumed to have deformed in use. With this correction, the estimate of error in normal pipet volume is 0.5 parts per thousand.

5.2. Elastic Stretching of Pipet

Circumferential and longitudinal stresses in a closed-end cylinder are, respectively,

$$S_c = kP/(R-1) \text{ and } S_l = P/(R^2-1), \quad (5.2-1)$$

where P is excess internal pressure, R is the ratio of external to internal diameters, and k incorporates both end-effects and relative behavior of thick walls. With modulus of elasticity E , relative diameters, lengths, and volumes are, respectively,

$$D/D_o = 1 + kP/E(R-1) \quad (5.2-2)$$

$$L/L_o = 1 + P/E(R^2-1) \quad (5.2-3)$$

$$V/V_o - 1 = (P/E)[(R^2-1)^{-1} + 2k(R-1)^{-1}]. \quad (5.2-4)$$

The temperature-dependence of E from [73] in $T^\circ\text{K}$ is

$$E = 1.15 \cdot 10^6 [1 - 4.35 \cdot 10^{-4} T], \text{ atm}, \quad (5.2-5)$$

and the behavior of k by comparison with [70, 74, 79] is

$$k = a(R-1)[(R^2+1)/(R^2-1) + m] = 1.11 \quad (5.2-6)$$

by introducing $R=3.2$, $a=1/3$ for end-effect and $m=0.3$ for Poisson's ratio. Within the accuracy of above estimates, therefore,

$$\lambda \equiv V/V_o = 1 + 1 \cdot 10^{-6} [1 + 4.35 \cdot 10^{-4} T] \cdot P_{\text{atm}}. \quad (5.2-7)$$

5.3. Thermal Contraction of Pipet

Thermal expansivity of copper [78] in the form $\alpha \equiv (L_o - L)/L_o$ as a function of temperature is used to compute a table of V/V_o versus temperature. For use with computing machines, this is fitted by a quadratic polynomial on the Kelvin temperature scale,

$$V/V_o = a + bT + cT^2,$$

$$V_o = 25.913 \text{ cm}^3; a = 0.990069; b = 1.667 \cdot 10^{-6};$$

$$c = 1.317 \cdot 10^{-7}. \quad (5.3-1)$$

6. Measurement of Amount of Sample

6.1. The Gasometer

The fluid contained in the pipet, the capillary, and the diaphragm cell is released into the gasometer system D (fig. 1). This is a set of spherical glass standard volumes in a precision water-bath thermostat, and a valve manifold with precision mercury manometer [48] in a circulating-air cabinet. Elevation of each arm of the leveled manometer is read to ± 0.05 mm by a highly reproducible lightbeam and photocell arrangement. A standard volume is selected such that the pressure is in the upper range of the manometer; i.e., 500 mm or greater. The instrument room temperature is controlled to about $\pm 0.5^\circ\text{C}$. To compromise between low obnoxious volumes and adequate pumping speeds, the manifolds are $\frac{1}{4}$ -in. copper tubing of 0.19-in. diam bore. For leak-free behavior, bellows-sealed valve seats and gaskets are a plasticized vinyl chloride polymer. Bellows volume increase per single turn is 0.15 cm^3 . This adds to standard volumes of 10 liters or more used for most determinations. Ionization gages serve for vacuum leak testing.

6.2. Gasometer Calibration

Volumes of the 1- and 2-liter spherical glass flasks are determined by weighing them with water on a 3-kg analytical balance against class Q weights. The 6-liter flask is weighed on a 20-kg single-beam platform balance against calibrated weight slugs. Adjustment is made for air buoyancy, water density,

and thermal expansion of the borosilicate glass [76]. Volumes at 300°K are given by the second column of table 1.

TABLE 1. Calibration of gasometer flask volumes

Nominal volume	Water weighing	Gas expansion	Assigned
1 L	994.48	ml (994.48)	ml 994.11
2 L	2,036.35	2,037.5 \pm 0.7	2,036.7
6 L	6,429.1	6,427 \pm 3.0	6,427
22 L		21,226 \pm 3.0	21,226
Ratio, 2 L/1L	2.0477	2.0488	

After determination of all manifold volumes including the manometer, the 2-liter flask is calibrated by gas expansion relative to the 1-liter flask; each successive flask then is calibrated relative to the sum of all smaller flasks. With all adjustments the results shown in the third column are obtained. Absolute volume standard is selected as the sum of volumes of the 1- and 2-liter flasks by water weighing, and the ratio of these two volumes by gas expansion is selected for assigning the values shown in the last column. Pressure-dependence of the flask volumes was computed from physical dimensions and mass of the individual flasks and the modulus of elasticity [76]. The nearly uniform results were confirmed experimentally upon a flask filled with water extending into a capillary neck,

$$(1/V)(dV/dP) = 1 \cdot 10^{-4} \text{ atm}^{-1}. \quad (6.2-1)$$

6.3. Adjustment for Capillary and Cell

The amount of sample in the pipet is the total amount behind valve 4 of figure 1, determined by gasometry, less amounts in capillaries and in the diaphragm cell under conditions of measurement for each P-T point. The rapid experimental method is justified provided these latter amounts can be estimated with sufficient accuracy. This is attained with a diaphragm cell volume which is small relative to the pipet, and by utilizing known and estimated gas-imperfection behavior of normal hydrogen.

A volume of 0.655 cm^3 for capillary tubing and diaphragm-cell exterior to the top of the cryostat and up to the pipet valve C-4 is obtained by weighing mercury out of the tubing and by finding differences with suitable gas-expansion methods. The quantity of hydrogen in these obnoxious volumes is computed from their temperatures, the pressure, and the compressibility factor for normal hydrogen [65].

The volume of the 71-cm-long, transition capillary from the top of the cryostat to the guard ring is $V_c = 0.0672 \text{ cm}^3$, or 0.26 percent of pipet volume. The amount of fluid in the capillary is computed by calculating the temperature T_x , corresponding to any position at a fraction x of capillary length from the ring at pipet temperature T_o to the top of the cryostat at room temperature T_1 , from thermal conductivity K of stainless steel [77] by the relation,

$$x = \left[\int_0^{T_x} K dT - \int_0^{T_o} K dT \right] \cdot \left[\int_0^{T_1} K dT - \int_0^{T_o} K dT \right]^{-1} \quad (6.3-1)$$

The number of gram moles of fluid in the capillary is

$$N_c = (PV_c/RT_o)\theta \quad (6.3-2)$$

where

$$\theta \equiv T_o \int_0^1 dx/T_x Z_x. \quad (6.3-3)$$

Indices o refer to the ring or pipet, x to relative position along the capillary, and $Z \equiv Pv/RT$ where v = molal volume. By known [23, 64, 68, 69] and extrapolated [3] data for Z , the capillary factor θ for hydrogen is determined at a sufficient number of sensitive points for smoothing, taking note of liquid-vapor discontinuities; results are summarized by figure 3. The ratio of amount of fluid in the transition capillary to amount in the pipet is necessary for an estimate of required accuracy. This ratio is $(V_c/V_o) \cdot \phi$, where $\phi \equiv Z_o \theta$ is summarized by figure 4. Due to the small value of V_c/V_o , a ten percent error in ϕ would correspond to a relative error well under 0.03 percent in density of the pipet sample at temperatures $\leq 100^\circ\text{K}$.

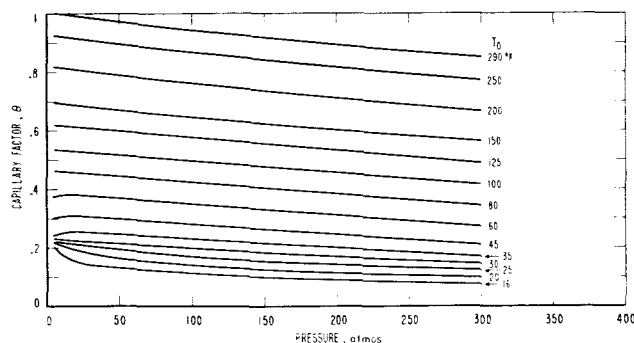


FIGURE 3. Capillary factor, θ .

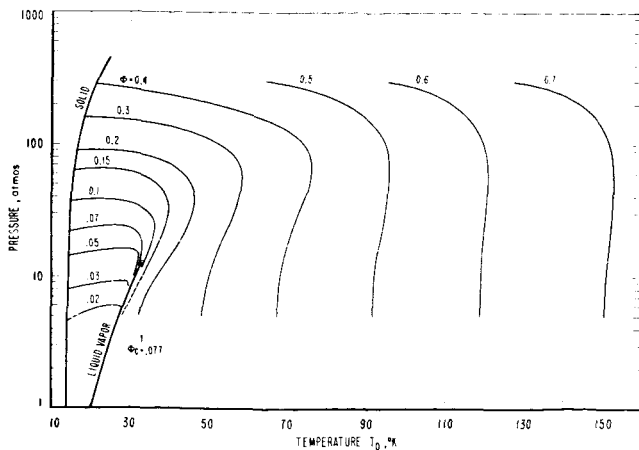


FIGURE 4. Capillary relative content, ϕ .

7. Measurement of Pressure

7.1. Piston Gage and Diaphragm Cell

The commercial, dual-range, precision, dead-weight gage and null-detector operate in the oil-filled F-manifold, figure 1 [52, 53, 57, 59]. The diaphragm, with adjustable electric contacts to indicate null position, is centered by use of an open-tube manometer. The oil pressure is adjusted to the experimental gas pressure with the screw-type oil press P. Prior to placing weights on the piston gage, the approximate pressure is read from bourdon gages.

Piston diameters of about 0.182 and 0.407 in. are measured with a light-wave micrometer to ± 5 millionths of an inch. Tolerance on the weights, determined by comparison with class S standards [54], decreases from 0.05 percent on the 1 psi weight to 0.002 percent on the 1000 psi weights. Adjustments to gage readings are made for temperature, pressure, acceleration of gravity, and barometric pressure. Observed sensitivity of pressure measurement with the small piston varies from under ± 0.05 psi below 500 psi to under ± 0.5 psi at 5000 psi.

As compared with known diaphragm-detectors [49, 61], the commercial instrument used here withstands extreme pressure imbalance without damage, but exhibits temporary hysteresis effects up to about ± 0.05 psi. A measured shift of null-point with absolute pressure is applied by the relation

$$P_{\text{gas}} = P_{\text{barom}} + (1.00002)P_{\text{oil}}. \quad (7.1-1)$$

Table 2 summarizes estimates of accumulated errors at different pressures.

TABLE 2. Estimates of accumulated pressure errors

Gage pressure, atm	2	20	200
	Error, atm $\times 10^3$		
Barometer.....	0.50	0.50	0.50
Diaphragm cell.....	4.00	4.00	4.00
Piston-cylinder diameter.....	0.06	0.60	6.00
Calibration of weights.....	.67	1.52	4.07
	5.23	6.62	14.57
Relative error $(\delta P/P) \cdot 10^3$...	2.6	0.33	0.073

Thermal equilibrium of the fluid sample, following a step-increase of temperature, is found by pressure observations to be established nearly as rapidly as the heating rate of the massive pipet. Occasional pressure balances are taken an hour apart to confirm this inference from the steady behavior of single observations.

7.2. Adjustment for Capillary Column

The column of cold fluid standing in the transition capillary tube produces an additional pressure P_c at the pipet,

$$P_c/P = JML_o\theta/RT_o$$

using symbols of section 6.3, pressure conversion factor J , molecular weight M , and capillary length $L_c=71$ cm. Since $JML_c/R=1.68 \cdot 10^{-3} \text{ }^\circ\text{K}$ for hydrogen, the adjustment for capillary column pressure is negligible.

8. Measurement of Temperature

8.1. Method and Instruments

The potentiometric method of figure 5 is employed with a 25-ohm platinum resistance thermometer calibrated by the NBS Temperature Physics section and a six-dial microvolt potentiometer [41, 42, 46]. The low-impedance, unsaturated standard cells are protected from occasional extreme temperatures of the laboratory by two concentric boxes of 1/2-in. aluminum in a plywood case [43]. The upper potentiometer current supply is stabilized by placing a lead-acid battery across an isolated, rectified, and filtered a-c source [60]. A 25-v, 200 amp-hr, thermally insulated and shielded battery, of a similar, low internal-discharging type, supplies the stable thermometer currents which flow in the calibrated precision standard resistors. The microvolt switch is wired so that the thermometer potential connections to the potentiometer can be reversed when the thermometer current is reversed. Microvolt galvanometer amplifiers with floating input circuits are coupled to 50- μ a panel galvanometers in suitable damping and range-changing circuits. To minimize spurious effects in the thermometer and thermocouple potential circuits, the continuous copper wires from the pipet in the cryostat are joined by a special solder [45] to untinned, copper cable wires near the cryostat on copper lugs in an iron-shielded, heavy aluminum box. The cryostat wires and shielded cables run in iron conduits. The cryostat and all electrical instruments are interconnected and grounded to the earth with heavy copper conductors.

8.2. Procedure and Calibration

When the instrument room air conditioner is started, spurious potentials up to ± 0.1 microvolt arise in the galvanometer circuit. These potentials

are observed by use of an internally-shorted emf position on the potentiometer and are bucked out at the galvanometer amplifier. When the cryostat is cooled with liquid hydrogen, a 0.35- μ v spurious potential, which is nearly independent of pipet temperatures up to 40 $^\circ\text{K}$ and increases with higher temperatures, appears across the thermometer potential leads in the absence of thermometer current. Potential measurements with reversed thermometer currents show the effect to be independent of current.

Thermometer currents are adjusted to exact integral milliampere values. To a corresponding, tabulated, thermometer potential is added the spurious thermometer potential to obtain a potentiometer dial setting yielding an automatically-controlled, integral-valued temperature. A thermometer current of 5 ma is used at temperatures below 35 $^\circ\text{K}$; 2 ma, from 35 to 75 $^\circ\text{K}$; and 1 ma, at 75 $^\circ$ and above. Thermometer heating by the 5 ma current produces an error of 0.0007 $^\circ\text{K}$ at 40 $^\circ\text{K}$. All measurements occur in the low range of the potentiometer.

The specified error limit of the potentiometer low range is 0.01 percent of reading plus 0.02- μ v. The calibrated value of the 1-ohm standard resistor is 0.99999 ± 0.00001 ohms. Apparently satisfactory agreement was found between the platinum thermometer calibration tables and measurements with above procedures for the ice-point and for vapor pressures of high-purity nitrogen and of parahydrogen, as described in section 11.

The accuracy of temperature measurements is summarized by table 3. It is based on the thermometer characteristic and currents, the potentiometer specifications, and a latitude of 0.05 μ v for bucking out spurious potentials. Thermometer calibration uncertainties are not included.

TABLE 3. Estimates of accumulated temperature errors

T, $^\circ\text{K}$	Thermometer			Potentiometer error, μv	Errors, δT , $^\circ\text{K} \cdot 10^3$		$\delta T/T$, $\times 10^4$
	i, ma	R, Ω	dR/dT		Potentiometer	External $\pm 0.05 \mu\text{v}$	
15	5	0.049	0.0074	0.045	1.22	1.35	170
20	5	.112	.017	.076	0.89	0.58	74
40	2	1.07	.075	.234	.62	.13	19
76	1	4.65	.109	.485	.89	.09	13
100	1	7.25	.109	.745	1.37	.09	15

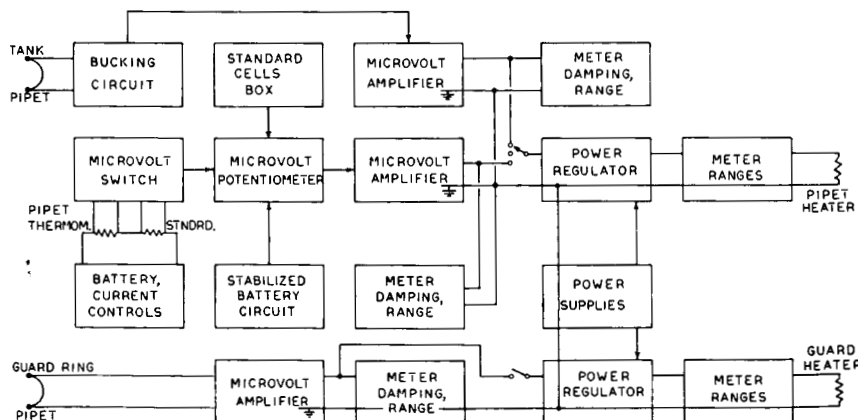


FIGURE 5. Temperature measurement and control methods.

9. Regulation of Temperature

Precisely controlled electric heating compensates for crudely adjusted, spontaneous cooling (section 4). The pipet temperature can be controlled [29] from a thermocouple, relative to the temperature of the refrigerant tank (upper left of figure 6), by a wide range microvolt bucking circuit, a microvolt amplifier [56] and a d-c power-regulator [50]. For all PVT measurements the pipet temperature is controlled from the platinum resistance thermometer and potentiometer. There is no perceptible noise at 0.0002 °K sensitivity. The accuracy of controlled temperature is equivalent to the described accuracy of measurement. To maintain a steady temperature during other operations with the potentiometer, the power regulator input signal switch is opened and the steady-state heating carefully adjusted by the power regulator control before undertaking such operations. If required, the above thermocouple control can be used. The guard ring temperature is controlled with similar instruments.

10. Computation of PVT Observations

10.1. Gasometry

The number, N , of gram moles of hydrogen contained behind pipet valve C-4 is calculated by the relation,

$$RN/P_m = [(EV_g + V_w)/T_w + V_a/T_a + V_b/T_b]/Z_{w,m} + V_o/T_o Z_{o,m}, \quad (10.1-1)$$

where P_m is mercury manometer pressure in atmospheres,

$$R = 82.057 \text{ cm}^3 \text{ atm/g mol deg } K,$$

$$P_m = KgDL_m, \quad (10.1-2)$$

$$K = 0.986923 \cdot 10^{-6} \text{ atm cm}^2/\text{dyne [4]},$$

$$g = 979.615 \text{ dyne/gram in this laboratory room,}$$

$$D = 13.5948 - 0.00245 \cdot t_m, \text{ g/cm}^3 \text{ [4]}, \quad (10.1-3)$$

$$t_m = \text{manometer mercury temperature, } ^\circ\text{C},$$

$$L_m = \text{manometer mercury height, cm (brass scale),}$$

$$E = \text{glass volume/pressure coefficient} \\ = 1 + 10^{-4}(P_m - 0.825), \quad (10.1-4)$$

$$T_a = \text{air-bath manifold temp, } ^\circ\text{K},$$

$$T_b = \text{NPD temp, } ^\circ\text{K},$$

$$T_o = \text{pipet temp, } ^\circ\text{K},$$

$$T_w = \text{water-bath temp, } ^\circ\text{K},$$

$$V_a = \text{vol of air-bathed manifold and manometer,} \\ 59.66 \text{ cm}^3,$$

$$V_b = \text{vol of lines, gasometer to C-valves, including} \\ \text{gage, } 22.37 \text{ cm}^3,$$

$$V_g = \text{vol of glass bulbs used, cm}^3,$$

$$V_w = \text{vol of water-bath manifold, } 13.00 \text{ cm}^3,$$

$$V_o = \text{vol of pipet, cm}^3,$$

$$V_o/T_o = 25.913[0.990069/T_o + 1.667 \cdot 10^{-6} \\ + 1.317 \cdot 10^{-7} \cdot T_o], \quad (10.1-5)$$

$$Z_{w,m} \text{ (at } T_w \text{ and } P_m) = 1.000044 + 0.000555 P_m, \\ (10.1-6)$$

$$Z_{o,m} \text{ (at } T_o \text{ and } P_m) = 1.0007 \\ - 1055/T_o^3 \text{ for } T_o \geq 40 \text{ } ^\circ\text{K.} \quad (10.1-7)$$

10.2. Pressure

The pipet fluid pressure P in international atmospheres is

$$P = 0.0680457 P_g + P_b \quad (10.2-1)$$

where

$$P_g = \text{deadweight oil gage pressure in psig,}$$

$$P_b = \text{barometric pressure in atm,}$$

$$P_g = k(g/g_s)[1 - 2.4 \cdot 10^{-5}(t_g - 20 \text{ } ^\circ\text{C})] [1 + \\ 4.2 \cdot 10^{-8} P_g] \cdot [\text{Nominal wt psi}]. \quad (10.2-2)$$

$$k = 1.00002, \text{ eq (7.1-1),}$$

$$(g/g_s) = 979.615/980.665,$$

$$t_g = \text{deadweight gage temperature, } ^\circ\text{C,}$$

$$P_b = KgD \cdot L_b \text{ as in eq (10.1-2),} \quad (10.2-3)$$

$$L_b = \text{barometer height, cm,}$$

$$t_b = \text{barometer temp, } ^\circ\text{C.}$$

10.3. Density

Density, σ , g moles cm^3 , is calculated by

$$\sigma V_o = N - (P/R)[V_c \theta/T_o + V_d/Z_d T_d] \quad (10.3-1)$$

where

$$T_d = \text{temperature NPD, } ^\circ\text{K,}$$

$$T_o = \text{pipet temperature, } ^\circ\text{K,}$$

$$V_o = 25.913 \lambda [0.990069 + 1.667 \cdot 10^{-6} T_o + \\ 1.317 \cdot 10^{-7} T_o^2], \quad (10.3-2)$$

$$V_c = 0.0672 \text{ cm}^3,$$

$$V_d, \text{ volume of NPD and warm capillary} = 0.655 \text{ cm}^3,$$

$$Z_d, \text{ for gas at } P \text{ and room temperature in } V_d \text{ is} \\ Z_d = 0.99990 + 0.000623447 P, \quad (10.3-3)$$

$$\lambda, \text{ eq (5.2-7),}$$

$$\theta, \text{ eq (6.3-3) and figure 3.}$$

11. Checks on PVT Calibrations

11.1. Thermometry Fixed Points

Vapor pressures of a commercial, high-purity nitrogen and of parahydrogen were measured prior to the PVT experiments. Examination of experimental technique later revealed failure to compensate some of the spurious potentials. Determination of these potentials provided adjustments, estimated accurate within 0.005 °C, which have been applied in preparing table 4.

TABLE 4. *Thermometry fixed point observations**

P, mm ^a	T _{obs}	T _{lit}	ΔT
Vapor pressure of nitrogen ^b			
625.05	75.732	75.730	-0.002
625.42	75.741	75.735	-0.006
626.03	75.744	75.743	+0.001
631.75	75.825	75.816	+0.009
631.68	75.826	75.815	+0.011
Vapor pressure of parahydrogen ^c			
626.33	19.639	19.632	+0.007
626.72	19.645	19.634	+0.011
626.90	19.650	19.635	+0.015
628.18	19.656	19.642	+0.014
629.12	19.656	19.646	+0.010

*All temperatures in deg K on NBS 1955 scale.

^a Mercury column height reduced to 0 °C at standard gravity.

^b G. T. Armstrong, 1954.

^c Hoge and Arnold, 1951.

11.2. Elevated Vapor Pressures

Initial PVT points of several runs were taken at saturation conditions to check instrumentation. If the substance is nearly pure parahydrogen, the observed pressure-temperature relations should agree with those of Hoge and Arnold. Table 5 presents

TABLE 5. *Elevated vapor-pressure observations*

P _{obs} , atm			Data from Hoge and Arnold ^a	
T °K	II	III	P, atm	dP/dT
22	-----	1.612	1.614	0.417
23	-----	2.069	2.071	.498
24	-----	-----	2.614	.587
25	-----	3.246	3.249	.685
26	3.978	3.983	3.985	.790
27	4.832	4.829	4.832	.904
28	5.785	5.792	5.795	1.026
29	-----	6.886	6.889	1.162
30	-----	-----	8.121	1.304
31	9.499	9.502	9.500	1.459
32	11.051	-----	11.047	1.643
32	11.051	-----	11.047	1.643
32	11.052	-----	11.047	1.643

^a Data of Hoge and Arnold interpolated to NBS 1955 temperature scale.

observed vapor pressures of parahydrogen from the series II compressed liquid runs and from the series III low-density runs in the vapor and gaseous region.

Data of Hoge and Arnold are interpolated to the NBS 1955 temperature scale of the present work. Temperature deviations corresponding to pressure deviations in series II range from 0.0098 deg at 28 °K to 0.0030 deg at 32 °K. The series III range is from 0.005 deg at 22 °K to 0.003 deg at 32 °K.

11.3. PVT Data for Normal Hydrogen

The first PVT run was made with normal hydrogen for comparison with known data, table 6. The

TABLE 6. *PVT observations on normal hydrogen*

T, °K	P, atm	v, cm ³ /mol	Z _{exp}	1.0026·Z _{exp}	Z _{lit}
28	30.869	30.443	0.4090	0.4101	0.4093 ^a
30	45.357	30.460	.5612	.5627	.5616 ^a
32	59.738	30.476	.6933	.6952	.6945 ^a
36	88.443	30.508	.9134	.9160	.914 ^{*b}
40	116.969	30.538	1.0883	1.0911	1.0902 ^b
45	151.884	30.574	1.2576	1.2609	1.259 ^{*b}
50	186.213	30.607	1.3892	1.3928	1.3928 ^b

^a Friedman and Hilsenrath, private communication.

^b Johnston and White, Trans. ASME **72**, 785 (1950).

*Nonlinear interpolation.

known data have been interpolated linearly except where indicated. Present results for Z in column 4 are multiplied by 1.0026 in column 5 as an adjustment for the pipet deformation which occurred at an unknown time during the experiments. Deviations of the former results are within 0.07 to 2.6 parts per thousand; of the latter within 0.00 to 2.2 parts per thousand.

11.4. Virial Coefficients

Corresponding to the virial equation,

$$Z = Pv/RT = 1 + B/v + C/v^2 + \dots, \quad (11.4-1)$$

the data function,

$$\phi = RT(Z-1)v = RTB + RTC/v + \dots, \quad (11.4-2)$$

exhibits satisfactory linear dependence on density at each temperature when the recalibrated pipet volume, $V_0 = 25.913$ cm³ is used for computation of experimental densities below critical. Unsmoothed values of RTB and RTC , determined by least squares, are given by table 7. These new data are equivalent to an equation of state for parahydrogen at densities up to 9 g mol/liter. For comparison are given values for normal hydrogen calculated from the smoothed table 19 of H. W. Woolley et al. [69], and values for RTB only, smoothed by us from the "smoothed" table CIV of A. S. Friedman [19]. Negative third virial coefficients in the latter table below 50 °K suggest that corresponding second virial coefficients are too small in absolute value. Our closely-spaced data suggest a so-called lambda-point maximum in the third virial coefficient at the critical temperature. The criteria of its validity have not been investigated. Concerning comparison of results, it recently has been shown that second virial coefficients for parahydrogen may be about 1 percent smaller in absolute value than for normal hydrogen at liquid hydrogen temperatures, in

agreement with these results [63]. Quantitative study of the ϕ -density behavior before and after correction of the pipet volume suggests accuracy of volumetric calibrations within one part per thousand.

TABLE 7. *Virial coefficients, parahydrogen*
Units of cm³, g mol, atm, deg K

T, °K	-RTB-10 ⁻⁵			RTC-10 ⁻⁶	
	Exp	(a)	(b)	Exp	(a)
24	2.229*	2.247	2.20	3.053*	-----
25	2.185*	-----	-----	3.432*	-----
26	2.139†	2.159	2.11	3.273†	-----
27	2.098	-----	-----	3.519	-----
28	2.059	2.075	2.02	3.647	-----
29	2.023	-----	-----	3.826	-----
30	1.987	1.996	1.95	3.938	-----
31	1.952	-----	-----	4.021	-----
32	1.917	1.921	1.88	4.096	-----
33	1.883	-----	-----	4.124	-----
34	1.848	1.849	1.81	4.110	4.171
35	1.814	-----	-----	4.103	-----
36	1.780	1.781	1.75	4.073	4.089
37	1.747	-----	-----	4.043	-----
38	1.714	1.715	1.70	4.020	4.020
39	1.683	-----	-----	3.998	-----
40	1.651	1.653	1.64	3.966	3.962
42	1.591	1.591	1.59	3.934	3.914
44	1.533	-----	-----	3.920	-----
46	1.478	1.473	1.49	3.922	3.846
48	1.423	-----	-----	3.929	-----
50	1.369	1.360	1.40	3.926	3.811
55	1.239	1.224	1.28	3.971	3.804
60	1.116	-----	1.16	4.074	-----
65	0.992	-----	-----	4.143	-----
70	.873	-----	0.94	4.232	-----
75	.762	-----	-----	4.414	-----
80	.647	-----	.65	4.514	-----
85	.531	-----	-----	4.587	-----
90	.417	-----	.40	4.688	-----
95	.310	-----	-----	4.849	-----
100	.205	-----	.14	5.007	-----

^a H. W. Woolley et al., J. Research NBS **41**, 379 (1948) RP1932, normal H₂.

^b A. S. Friedman, Ohio State dissertation (1950), normal H₂.

*Based on only two data points.

†Based on only three data points.

12. Comments on Overall PVT Accuracy

Requests for a statement of overall accuracy of data in the form $Z \equiv Pv/RT$ are commonplace. This accuracy depends not only on calibrations, but also on all the adjustment computations and the particular conditions defining the state of the fluid. The relative error in Z is the sum of relative errors in experimental variables,

$$\frac{\delta Z}{Z} = \frac{\delta P}{P} + \frac{\delta v}{v} - \frac{\delta T}{T}$$

Estimation of pressure errors is indicated by section 7.1. and table 2. The complexity of error estimates for molal volume, v , is appreciated by reference to eq (10.3-1). In view of sections 5 and 6, table 1, and the unpublished details of calibration and adjustment of obnoxious volumes, we venture the experimentalist's opinion that error in v generally is under two parts per thousand. Temperature errors, in view of tables 3, 4, and 5, are within 0.02 °C except near 14 °K, comparable to uncertainty in the low temperature scale [38]. Value of the gas

constant used for present computations is $R=82.057$ cm³ atm/g mol deg. It may be noted that at high densities, any isotherms of pressure as a function of density are highly sensitive to errors in density, due to the relatively incompressible state of the fluid, a situation giving spurious indications of low precision in the measurement of pressure.

13. Calorimetric Apparatus

13.1. Introduction

Measurements of the volume, mass, and temperature of a fluid sample are necessary to define the state corresponding to each specific heat determination. For high pressures the PVT pipet must be massive so that its volume will be calculable. The PVT data are obtained first because they are used for calibration of the volume of the thin-walled calorimeter as a function of temperature and pressure. Calorimetric methods have been reviewed [29] and the calorimetry of some compressed fluids described [28, 30, 33, 34, 35, 36]. The purpose of this section is to provide a brief description of some improved instrumentation and of the integration of calorimetric with PVT apparatus. Calorimetric calibrations will accompany the publication of results.

13.2. Cryostat and Calorimeter

The calorimeter resides in an additional cryostat of basic construction identical with that for the PVT pipet, with the high-pressure hydrogen capillary, vacuum, and liquid-transfer plumbing in parallel through suitable valves. Alternation of experiments requires no dismantling. Figure 6 is the calorimeter region of the cryostat, and figure 7 is the calorimeter section. All parts are copper except for

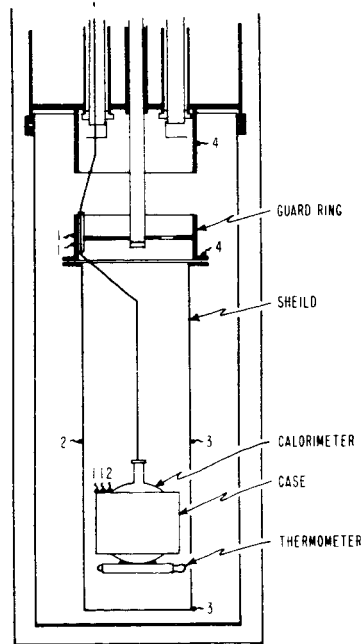


FIGURE 6. *Calorimeter region of calorimeter cryostat.*
(Shield is misspelled in the above figure.)

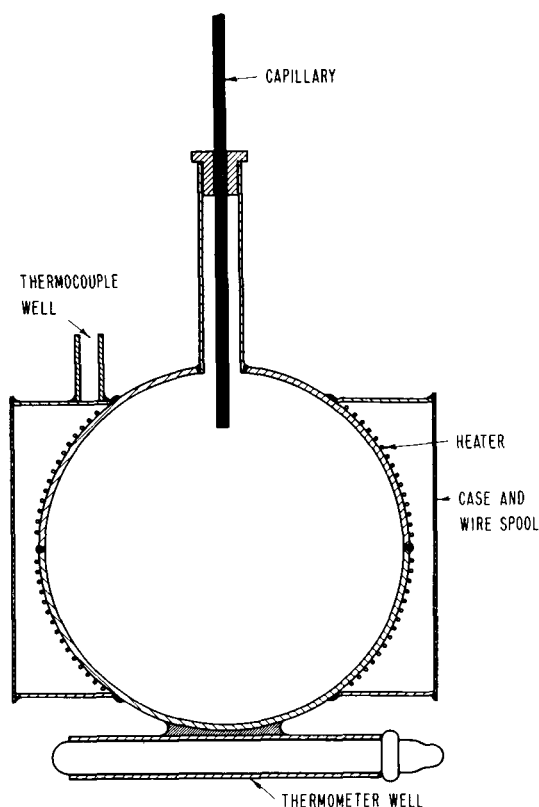


FIGURE 7. Calorimeter section.

sphere, capillary tube, and the guard-ring support tube. The 2-in. diam, type 316 stainless steel, spherical calorimeter has a nominal wall thickness of 0.06 in. It is fabricated from spun hemispheres, welded together, with addition of a 1-in.-long neck of $\frac{1}{4}$ -in. tubing. The spherical shape is improved by expansion with water pressure. Yielding to a permanent volume increase of 10 percent was observed with a pycnometer surrounding the calorimeter. It occurred at pressures from 5,000 to 6,400 psi, corresponding to metal stress roughly 8.3 times these values. Elastic behavior following this deformation was $\Delta V/V\Delta P = 1.59 \cdot 10^{-5} \text{ atm}^{-1}$, corresponding roughly to a circumferential modulus $(3d/4t) V\Delta P/\Delta V = 23 \cdot 10^6 \text{ psi}$, where d is diameter and t is wall-thickness. After electroplating copper inside and outside to about 0.2 mm thickness, avoiding sulfate electrolytes, the normal volume is 72.35 cm^3 , determined by gas expansion from the calorimeter in the cryostat. The 100-ohm, constantan wire heater is varnished directly onto the sphere, and shielded by the lightweight calorimeter case, which serves also as the wire spool for thermally anchoring thermocouple and thermometer lead-wires. The $\frac{1}{16}$ -in. o.d. stainless steel capillary has a bore diameter of 0.0345 cm. This relatively large bore is essential for rapid filling and emptying of the calorimeter. Volume of this capillary, including a valve at the head of the cryostat, is 0.080 cm^3 .

Adiabatic shielding is in two parts: the guard ring, and attached, lightweight shield can. The ring tempers all electric wires, pressed into individual, longitudinally machined grooves. These wires lead from similar grooves in the cold ring and lead to the calorimeter case. Separate heaters are wound on the guard ring, the cylindrical surface of the shield and as a plane spiral on the bottom of the shield can. The two shield heaters operate in a divider circuit from a single regulator. These heaters are automatically controlled from thermopile 1 and thermocouple 2 respectively of figure 6. Thermocouple 3 serves for manual adjustment of the side-to-bottom heat divider. Thermocouple 4 serves for automatic temperature control of shields and calorimeter, during gas-expansion calibrations of the calorimeter volume, with reference to the refrigerant tank temperature.

To facilitate control of the calorimeter temperature during some calibrations, a small heat leak is introduced to the present apparatus. Thermal contact between electric wires and tempering ring is reduced to obtain the calorimeter cooling drift described in section 13.4. The calorimetric method therefore may be described as quasi-isothermal.

13.3. Control and Measurement of Heat

The control circuits for calorimetric heating are indicated by figure 8. Although they are conventional in principle, a useful simplification is application of an electronic battery: a 0.5 amp, transistorized, d-c power supply, continuously adjustable to 0.02 v from 0 to 32 v, with regulation and stability better than 0.002 v. The rms ripple is 0.001 v. The battery source impedance, R_b of the figure, is readily adjusted equal to the calorimeter heater resistance when the battery potential indicated by $P-1$ is twice the heater potential indicated by $P-2$ [31]. To provide time for potentiometric measurements of the heater power, and for shield temperature adjustments, a temperature rise of about 2° in a fixed interval of 10 min at all temperatures is realized by adjusting the battery potential. This adjustment does not affect R_b , in contrast to behavior with conventional batteries and rheostats. Relay coils are operated with direct current to reduce induction of spurious a-c effects in the low-level circuits.

Potentials are measured with the 6-dial microvolt potentiometer and with a type K-3 universal potentiometer, each indicating through an electronic galvanometer [56], as in figure 5. Potentials to be measured are connected to each potentiometer by high-quality, commercial, microvolt selector switches. Four measurements of heater potential and current are made in 10 min. Heater power is constant to better than 1 part in 10,000. The standard electric, clutch-type, synchronous stopclock utilizes local, 60 c/s, powerline frequency for the time standard. The NBS Time Standards Section finds that this frequency usually is accurate and constant to well within 0.03 percent.

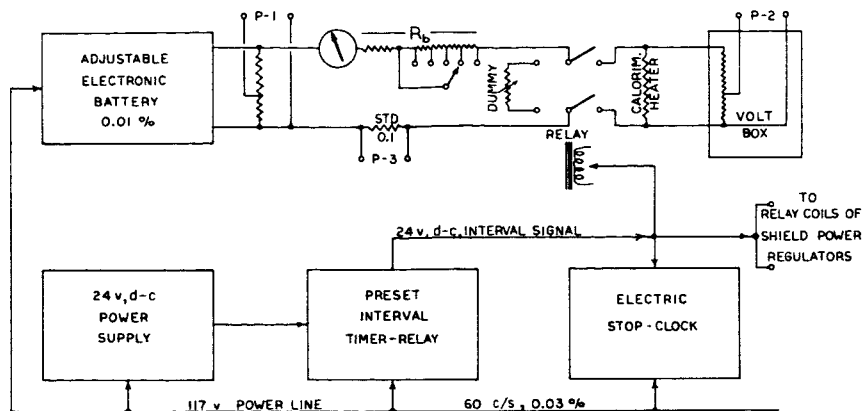


FIGURE 8. Calorimetric heat control methods.

13.4. Measurement of Temperatures

The calorimeter platinum resistance thermometer is calibrated and the thermometric technique checked as described for PVT determinations. Imperfections of adiabatic shielding yield empty calorimeter drift rates from $-0.0009^{\circ}/\text{min}$ at 20°K to $-0.0019^{\circ}/\text{min}$ at 100°K . These are linear in time.

Five temperature observations in 5 min precede a heating interval. Nonlinear equilibration following the interval requires a few minutes, and is observed with a recorder. Five similar temperature measurements follow. Temperature-time behaviors are extrapolated to mean time of the heating interval, by a least-squares computer program, at which time is taken the calorimetric temperature increment.

13.5. Control of Shield Temperatures

The different methods, isothermal and adiabatic shielding, are useful for different purposes [37]. The adiabatic method is selected here for rapid adjustments in the range 20 to 100°K where thermal transport is almost entirely conductive. Gold-cobalt versus copper thermocouples indicate temperature differences between the calorimeter and the guard ring and shield respectively. An individual regulating system is employed for each of the latter. An improvement of present instrumentation, indicated by the bottom row of figure 5, is its simplicity relative to current practices [27]. Control instruments are the microvolt amplifier [56] and the power regulator [50]. Two factors contribute to satisfactory operation. (1) Thermocouples are so placed on shields as to give rapid but average response. The heater windings and powers are designed to match the areas and masses of metal to be controlled. (2) The power regulator contains a solenoid relay, operated by the heating interval signal, figure 8, which automatically boosts the shield heating to a manually pre-set level. This eliminates the delay otherwise required for development of the temperature difference normally utilized for automatic control. The booster circuit does not affect the low output impedance of this regulator, thereby

avoiding the loss of power-gain and temperature-regulation otherwise suffered when resistances or other impedances are inserted in the heater circuit for boosting control. Because automatic resetting instruments are not necessary for the present work, the normal steady-state heating also is manually adjusted at the power regulator. For calibration work, the shield versus calorimeter temperature differences may be recorded from the microvolt amplifier output signals by means of simplified strip-chart instruments. A typical chart shows that, with routine error in adjustment of the boost heat level, the guard ring-versus-calorimeter temperature difference peaks at 0.001°C at the start of an interval and decays to within 0.0001° in 20 sec. The same behavior with opposite sign follows the ending of an interval. Relative change in the steady heat-leak over the copper wire bundle between guard ring and calorimeter is negligible during a heating interval.

The numerous machined parts for the cryostats were made in the NBS, Boulder shop under S. Landis. The skillful assembly and silver-soldering of these parts as well as the construction of the liquid transfer and hard vacuum systems by Cryogenic Division instrumentalist W. R. Bjorklund greatly advanced the project. D. E. Diller placed all of the small electric wiring in the cryostats, intercalibrated the gasometer glass volumes, performed the gas-expansion calibrations of the pipet, checked fixed-points of the platinum thermometer, and measured null-point shift of the diaphragm cell in addition to other important contributions. L. A. Weber assisted with the many details of placing the PVT apparatus in final operating condition. B. A. Younglove determined mechanical properties of the calorimeter and with D. E. Diller placed the calorimetry in successful operation. Hans M. Roder, in programming the computer work, devised subsidiary equations presented in sections 5.3 and 10. Continuing encouragement from Robert J. Corruccini and Russell B. Scott have been essential in bringing this long task to completion.

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(Paper 65C4-76)